Green Synthesis of Iron OxideNanostructures

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by

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CERTIFICATE

This is to certify that the thesis entitled "**GREEN SYNTHESIS OF IRON OXIDE NANOSTRUCTURES**", submitted by Debasis Nanda (213CH1124) in fulfillments for the requirements for the award of Master of Technology Degree in Chemical Engineering at National Institute of Technology, Rourkela (Deemed University) is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/ Institute for the award of any Degree or Diploma.

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Date- 25/05/2015

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Abstract

Iron oxide nanoparticles are continuously drawing researchers' attention because of their unique electronic and physiochemical properties in the fields of catalysis, environmental remediation, bio-imaging, and drug delivery, and so on. Iron oxide nanoparticles are mainly prepared by the chemical reduction of iron precursors, but the environment toxicity and expensiveness of reducing agent limits its application. Recently many people reported the leaf extract as a reducing agent for the synthesis of the variety of NPs as economical, environmentally friendly, and biocompatibility source. In this study, we report a simple, low cost, time-consuming and environment-friendly synthesis of iron oxide and iron oxide/Au coated nanorods using green tea extract as a reducing agent. On the other hand, iron-oxide tubes were also synthesized by a heat treatment method using a cotton template. The as-synthesized particles were characterized by UV-vis spectroscopy, FTIR spectroscopy. The crystalline structure and the phase change were clarified by XRD. The FESEM analysis revealed the morphology of the synthesized nanoparticles. The average surface area of the microtubes synthesized was found to be 72 m^2/g from BET. The synthesized nanoparticles were used as Fenton as a catalyst for organic dye degradation, reduction of 4-NP to 4-AP and Oxidation of THF.

Keywords: Nanorods, green synthesis, Tea extract, Microtubes, Au/Fe_2O_3 Nanorods.

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Abbreviation

UV-vis: Ultra-violet visible

FT-IR: Fourier Transform Infrared

XRD: X-ray Diffraction

FESEM: Field Emission Scanning Electron Microscope

TEM: Transmission Electron Microscope

JCPDS: Joint Committee on Power Diffraction Standards.

$FeCl_3$: Ferric Chloride

$HAuCl_4$: Chloroauric Acid

NPs: Nanoparticles

NRs: Nanorods

pH: Potential of Hydrogen

MRI: Magnetic Resonance Imaging

EGCG: Epigallocatechin gallate

4-NP: 4-Nitrophenol

4-AP: 4-Aminophenol

MB: Methylene Blue

CHAPTER-1

Introduction

1.1 Introduction:

In nanotechnology, the particles are defined as a small object that acts as a whole unit with respect to its transport and properties. Nanotechnology is a multidisciplinary branch of science which deals with synthesis, analyze nanomaterials and their novel properties that is different from the bulk material from which it is produced, and thus lead to many applications ranging from biomedical[1]–[4] , waste treatment [5], electronics[6], catalysis[7], [8], sensors[9] etc. Nanoparticles (NPs) are particles between 1 to 100 nanometers in size. The nanoparticles may be metals, semiconductors or insulators. The NPs are of great interest because of their unique properties such as mechanical, structural, melting point, Electrical conductivity, Optical, and Magnetic. Some examples cited are the elastic module reduces dramatically with the reduction in size to nanoscale and the hardness increases with decrease in size. Similarly, the melting point decreases with a reduction in particle size because melting starts from the surface and with size reduction the surface to bulk atom ratio increases. Electrical conductivity decreases as the resistivity increases. The nanoparticle has a different geometry, ranging from zero to three dimensions such as nanoparticles (0D), nanograins (0D)[10], [11], nanoshells (0D)[12]–[14], nanorods (1D)[15]–[17], nanotubes (1D)[18], [19], nanowires (1D)[20] , superlattices (2D)[21] are some of the examples. Nanoparticle can be synthesized in two ways:-

a. Bottom-Up Approach:

In this approach atoms and molecules are assembled to form nanomaterials of required size and shape by controlled deposition or reaction parameters. The example of such approach is in the electronics industry in making integrated circuits (IC), sol-gel, etc.

b. Top-Down Approach:

In this approach, the reverse mechanism is used where the atoms and the molecules are removed from the bulk material to obtain desired nanoparticle.

Different types of nanoparticles are synthesized by these approaches such as metallic NPs, Non-metallic NPs, metal oxides NPs, bimetallic NPs, core/shell NPs, etc. Metallic nanoparticles are of great interest because it shows Surface Plasmon Resonance Phenomenon [22] where the surface electrons of the metal capture the light incident on it and reflect with another wavelength thereby giving different colors. The metallic NPs can be divided into Noble metals (gold,

platinum, palladium and silver) which are more stable and the other type are Magnetic nanoparticles (Iron, Nickel, and Cobalt) which are mainly ferromagnetic substances. Magnetic nanoparticles are studied in details due to their different applications.

Magnetic nanoparticles are mainly made of Ferromagnetic elements such as Iron, Nickel, and Cobalt. Nowadays, these nanoparticles have attracted the focus of researchers because of their tremendous applications including environmental remediation [5], [23], [24], biomedical applications[1], [2], data storage[6], sensors[25], catalysis[7], [8], [26], etc. The applications are possible because of their high surface to volume ratio that changes the ferromagnetic particles to superparamagnetic particles. For this reason, the coercivity loss is neglected theirs by retaining the properties of the metallic Nanoparticles. Magnetic NPs mainly iron is of great interest because it's cheap, easily available and shows more magnetic properties than other metallic elements. The nanoparticles of iron are primarily iron oxides because iron nanoparticles are very much unstable in the atmosphere for which its gets converted to iron oxide very quickly to attend stability. The one-dimensional iron oxide nanoparticles mainly nanorods and nanotubes are dominated from their counterpart zero-dimensional iron oxide nanoparticles because of their high surface to volume ratio for which they give better results in different applications.

1.2 Objective:

In this study, we have Novel synthesized simple, eco-friendly way to iron oxide nanorods, iron oxide tubes, and Au coated iron oxide nanorods. Green Tea extract has been used as the reducing agent for the synthesis. Cotton is used as the template for the tubes. The synthesized NRs were then used as catalyst for the oxidation and reduction of organic solvents. The tube was used as a Fenton-like catalyst for the environmental remediation purpose.

CHAPTER-2

Literature Review

In past, many researchers have performed their works on synthesis, characterization and application of the iron oxide nanoparticles because of their unique property of superparamagnetic property [28], high surface to volume ratio and their reusability. The use of iron oxide nanoparticles in different applications is because for their lost cost and easy way to synthesis. The synthesis of iron oxide nanoparticles are done by various methods, some of them are chemical reduction- precipitation method, co-precipitation method (under oxygen-free condition), Micro-emulsion method, Chemical Solution Method, Modified co-precipitation Method, Thermal Decomposition, Borohydride Method, Sol-Gel Method, cyclic chemical synthesis process, modified solve- thermal method and Reduction Method [28]–[31]. Most of the study has been reported based on the reduction of iron salt precursors to form iron oxide Nanoparticles. The precursors that are mainly used for the synthesis are Ferric Chloride, Ferrous Sulphate, organometallic like iron carbonyl, sty-DVB copolymer, nitrate nonahydrate, RAFT Agent 2-Propanoic Acid and Ammonium Iron(II) Sulfate. Different ratios of precursors are also been used for the synthesis process for example Ferric Chloride to that of Ferrous Sulphate are mixed at a ratio of 2:1. These salt precursors were reduced mainly by chemical reagents Sodium Borohydride, long-chain amines, amino acids, hydrazine and lithium borohydride and surfactants like CTAB, polymers. Due to their disadvantages such as their ill effect on environment leads to the discovery of new and better methodology of synthesis of iron oxide nanoparticles called green method. In this methods different parts of the plants such as leaves, fruits, flowers, etc. are used as the reducing agents. There have been many reports of the synthesis of the iron oxide nanoparticles help of Green Tea Extract, Black Tea extract, oolong extract, mango leaves, cloves, rose leaves, neem leaves, etc. The polyphenols that are present in the green plants help in reducing the salt precursors to iron nanoparticles but as they are very much unstable they form iron oxide when synthesized in open atmosphere. In the case of the microorganisms, it has been studied that the proteins that are present are responsible for the reduction of the precursors. The other conditions such as pH, reaction rate and temperature were also considered, and mechanisms for the formation of different shape and size of the iron oxide nanoparticles were also being discussed. For example, the effect of the pH range 9.7 to 10.6 tends to contain pure magnetite, and maghemite and geolite tend to appear in pH below 8.5. The iron oxide nanoparticles that are synthesized are used in many applications are discussed earlier.

The study of the nanoparticles by the researchers' were focused on one-dimensional nanoparticle such as nanorods, nanotubes, nanobelts, etc. have different properties such as more surface to volume ratio from their counterparts i.e. zero-dimensional nanoparticles. Different metals such as iron, gold, copper, zinc etc., nonmetals such as gallium nitride, carbides etc. and metal oxides like iron oxide, zinc oxide, copper oxide etc. nanorods has been synthesized and studied for different applications This unique property had increased their need in various fields of applications such as waste water treatments[24], [30], [31] and the more surface area gives more active sites for catalysis [32], photocatalysis [33], lithium-ion batteries [34]etc. The increasing demand for the study of the iron oxide nanoparticles in the recent years had increased because of their semiconductor property and superparamagnetic property. Thus, the combination of both the factors make researchers shift their studies to the one-dimensional nanoparticle. The one-dimensional iron oxide nanoparticles mainly nanorods synthesis used different methods like solvo-thermal method[35], hydrothermal method [24], [36], sol-gel method[15], Iron-water reaction[37], etc. The study of the various parameters such as temperature, pH, salt precursors and the reducing agents used are also reviewed that favors the formation of iron oxide nanorods.

Besides nanorods, many studies have been done on the iron oxide nanotubes. The tubes being hollow in nature have a right surface area and porosity than the rest of the nanoparticles. The researchers have used different metals [38], [39] and non-metals[40], [41] for the synthesis of the nanotubes. The iron oxide nanotubes are of great interest because of its easy availability, low-cost and due to their different unique properties such as for semiconductor property and magnetic property. The iron oxide tubes owing to these unique properties have many applications such as Lithium-ion batteries [41], [42], catalyst [43], [44], drug delivery[45], sensors[46], photocatalysis[47]–[49], water splitting[50], etc. Different methods such as electro-deposition[46], [47] , hydrothermal method [18], [39], [43], [51], heat treatment method, Mahe-break-mix process[19] etc. The synthesis of the nanotubes is also done by using different templates like alumina membrane, zinc oxide arrays, polycarbonate membrane, etc.

Nobel materials are of considerable interest because of their properties of non-reacting nature for which they can be used again and again without losing their properties. The Nobel Nanoparticles have a unique property of Surface Plasmon Resonance (SPR) in which they absorb different spectrum of light according to their particle size and reflect different colors. The non-

toxic, inert nature and SPR properties of the gold make its application in the field of biomedical applications such as anti-cancer[3], thiamine detection[9], etc. and also used as the catalyst[54] applications. These applications found suitable and more efficient when the particle size gets reduced. Due to small particle size the surface to volume ratio increases. But it has been discovered that after a certain size, the recovery of the gold particles cannot be possible. This problem leads to the formation of the supported catalyst. Different materials are used as the supported catalyst for the gold. To name a few are carbon[53], block polymer micelle[54], TiO_2[55], Ceria[56], Iron-oxide [57]–[59]etc. From the synthesis point of view different method such as co-precipitation method[60], template basis[53], dip coating method[54], wet chemical method[59], hydrothermal method[60], etc. have been used. These Au supported catalyst were used in biomedical applications[58], [60], [61], catalysis[57], [62], water-gas shift reactions[56], oxidation of glucose[53], etc. The interest of focus has been shifted more to the iron oxide supported Au catalyst because of its superparamagnetic property, low cost, easy availability.

CHAPTER-3

Experimental Work

Experimental Work:

3.1 Materials and Method:

The Green Tea was brought from the farms of Darjeeling. The metal precursors used in this experiment were Ferric Chloride Anhydrous from Merck. For the application purposes the gold precursor used, was $HAuCl_4$, H_2O_2 of (30% (v/v)) and Methylene Blue were from Merck. 4-Nitrophenol and THF from Loba. The cotton used as the template for the synthesis of iron oxide tubes were from the local market. In synthesis or solution preparation, the ultrapure water of 18.2 mΩ cm resistivity was used.

3.2 Preparation of Green Tea Leaf Extract Powder:

The extract of the tea was prepared by taking 50 g of tea in 300ml of Millipore water. The solution was heated at 80 °C in the microwave-reflux method to get the tea extract. The extract was then collected and centrifuged at 10,000 rpm for 10 min to remove the suspended tea particles. The centrifuged supernatant tea solution were dried into to powder form by the help of a freeze dryer. 1% (w/v) solution was prepared from the tea powder to carry out the experiment.

3.3. Synthesis of Iron Oxide Nanorods:

A 10mM stock solution was prepared by mixing 0.0162g of $FeCl_3$ in 10ml of ultrapure water. The stock solution was diluted to 1mM strength for the synthesis of iron oxide nanorods in 10ml solution. 1ml of the stock solution was added to 7.5 ml of water and was stirred for 5 min, to which 1.5 ml of tea extract was added i.e. 0.15% (w/v) strength of tea. On addition to it the color of the solution changed from yellow to dark greenish black color immediately confirming the synthesis of the iron oxide nanoparticles at ambient temperature. The solution was then heated to 80ºC in the microwave so that the particles gets settled quickly. The particles synthesize then centrifuged and were washed with ultrapure water and ethanol to remove the excess precursors or polyphenols present and were dried to powder in freeze dryer for characterization and application purpose.

3.4 Synthesis of Au coated Iron-oxide Nanorods:

A 10mM stock solution was prepared by mixing 0.0162g of $FeCl_3$ in 10ml of ultrapure water. The stock solution was diluted to 1mM strength for the synthesis of iron oxide nanorods in 10ml solution. 1ml of the stock solution was added to 7.5 ml of water and was stirred for 5 min, to which 1.5 ml of tea extract was added i.e. 0.15% (w/v) strength of tea. On addition to it the color of the solution changed from yellow to dark greenish black color immediately confirming the synthesis of the iron oxide nanoparticles at ambient temperature. The $HAuCl_4$ was also added to the solution with tea so that it gets reduced and get coated on iron oxide nanorods. The particles synthesize then centrifuged and were washed with ultrapure water and ethanol to remove the excess precursors or polyphenols present and were taken for characterization and application purpose.

3.5 Reduction of 4-Nitrophenol by Au coated Iron-oxide Nanorod:

The sample was prepared by adding 4-NP (0.1 mM) strength in the beaker. To it 500µl of $NaBH_4$ (100mM) was added which changed the color from pale yellow to dark yellow. 0.33 mM concentration of catalyst and rest Millipore water to form 5 ml of solution. The reaction started when the catalyst was added to it, and the sample was collected at regular interval till the color of the sample became colorless. The collected sample was taken for characterization for further verification.

3.6 Synthesis of Iron oxide tubes:

A 10mM stock solution of $FeCl_3$ was prepared by mixing 0.0162g in 10ml of ultrapure water. The cotton that was taken as the template was first isopropyl alcohol to remove all the foreign impurities that are present on its surface and beneath and was dried in the oven. Then the dried cotton was soaked in tea extract for 5 min and then squeezed to remove the excess tea content from it. Then the cotton was soaked in the iron salt precursor solution. On dipping, the color of the cotton changed to blackish and was kept for 5 min in the solution. The sample was then dried in an oven for 2 hrs and then was heated at 450ºC for 2 hrs in the furnace. After 2 h, the sample was cooled and collected for characterization and application purpose.

3.7 Degradation of Methylene Blue by Iron-oxide tubes:

A solution was prepared by addition of 0.1 mM strength of MB. To the sample 80mg/l of catalyst and 2ml of 30% (v/v), H_2O_2 was added at a time. After the addition, the reaction was started, and the sample were collected at each interval to study the degradation of MB. The collected samples were taken for characterization to examine the degradation of the sample by the catalyst.

3.8 Characterization:

The morphology and size were verified by characterizing the sample by FESEM and TEM analysis. BET analysis was done to determine the surface area of the tubes. XRD and UV-vis have been done to verify the crystalline phase and adsorption measurement respectively. The study of the functional groups was done by FT-IR analysis.

CHAPTER-4

Results and Discussion

Results and Discussion:

4.1 Reduction Mechanism of Green Tea:

Green tea is taken as the reducing agent for the synthesis of the different morphology of iron oxide nanoparticles because it contains a high amount of polyphenols and other organic groups in it. It has been found out that about 4000 species are present out of which 1/3rd of the total is polyphenols[63] that help in the reduction of the salt precursors to nanoparticles. The polyphenols consist of flavonoids and catechins. The catechins mainly the Epigallocatechin gallate (EGCG) is the active catechin that take part in reduction process because it has a standard potential of 0.57V that can thus reduce the Fe^{3+} to Fe^{0} as the standard potential of the iron is -0.036 V. In further study it was found that the Epigallocatechin gallate (EGCG) consists of number of aromatic rings out of which a group called gallic acid denoted by (B and D in figure) of phenyls type takes parts in the reduction process. The reduction mechanism takes place in two steps first when the precursor is added it first forms a complex by breaking the –OH bond and forming a partial bond with a metal ion. Secondly, there is breakage of the partial bond and the transfer of electrons to reduce the metal ions to nanoparticles, and thus itself get oxidize to ortho-quinone that has been shown in the figure.

$$nFe^{3+} + 3Ar–(OH)_n \rightarrow nFe^{0} + 2nAr= O + 2nH^{+} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

Where Ar is the phenyl group, and n is the number of hydroxyl groups oxidized by Fe^{3+}.

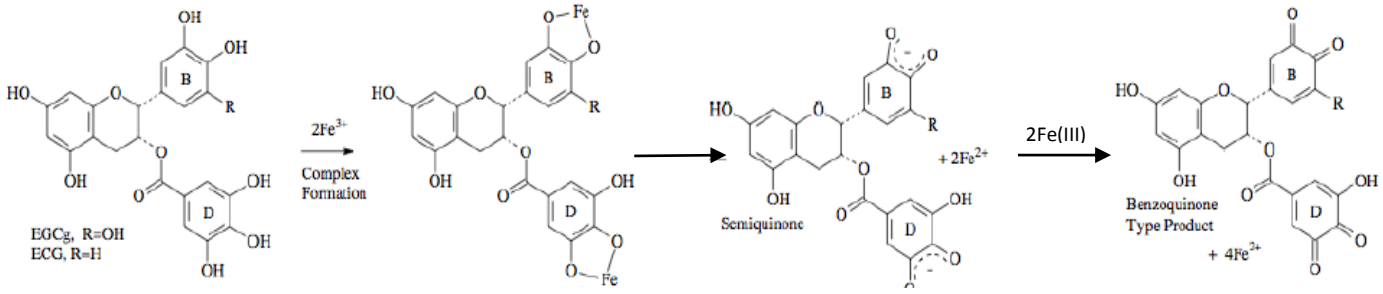

Figure 1: Two-step mechanism of reduction of the iron salt precursor by green tea extract.

The mechanism can also be explained by the FT-IR analysis of the tea extract and the iron oxide nanorod as shown in Figure2. This gives us an idea to determine the functional group that is responsible for the reduction. The absorption band were taken from 1000-1800 cm^{-1}. The bond vibration of the tea extract was found out at 1683, 1623, 1362, 1213 cm^{-1}. These bands represent the bonds –C=C-C=O and –C=C- in rings of aromatic groups, -C-C- in ring aromatic group, C-O-stretch of eaters and ethers group and –C-O stretch of polyols group of catechins respectively. After the reaction, the C-O stretch disappears which may be due to the involvement in the reduction of the precursor.

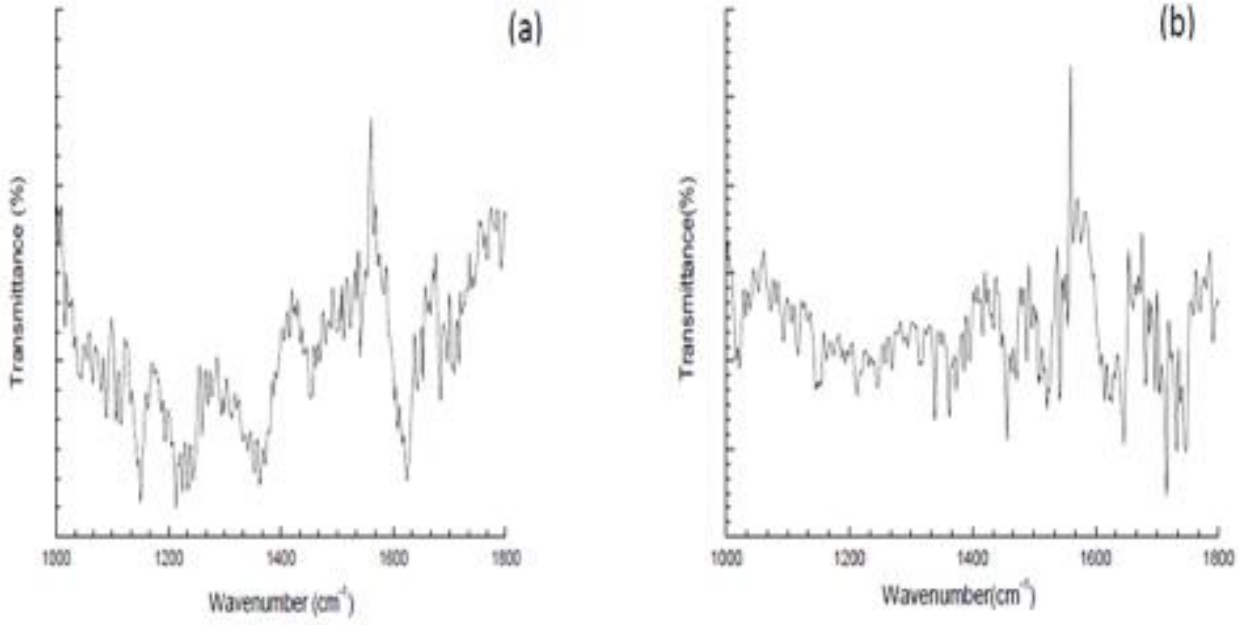

Figure 2: FT-IR of (a) Tea extract, (b) Iron oxide Nanorod

4.2 Iron Oxide Nanorod

Iron oxide nanoparticles are of interest in the research because of their unique properties of electrical property, optical properties, etc. Besides these properties due to the other factors like low cost, easy availability makes it more useful for different applications. It has been also seen that the properties of the particles depends on the size and morphology of the particles. Thus, nanorods are very much advanced than that of the nanoparticles because of their high surface to volume ratio.

4.2.1 Morphology study of iron-oxide Nanorods

The size and the morphology of the synthesized product were a confirmation to be rod-shaped by FESEM and TEM analysis as shown in Figue3. It has been observed that the rods formed are of length 130-150nm and width of around 20nm from FESEM as in figure3 (a). The density of the particles can also be seen from Figure3 (b). From TEM figure3 (c,d) the perfect rod shape coated with a layer of polyphenols of 2nm width can be observed.

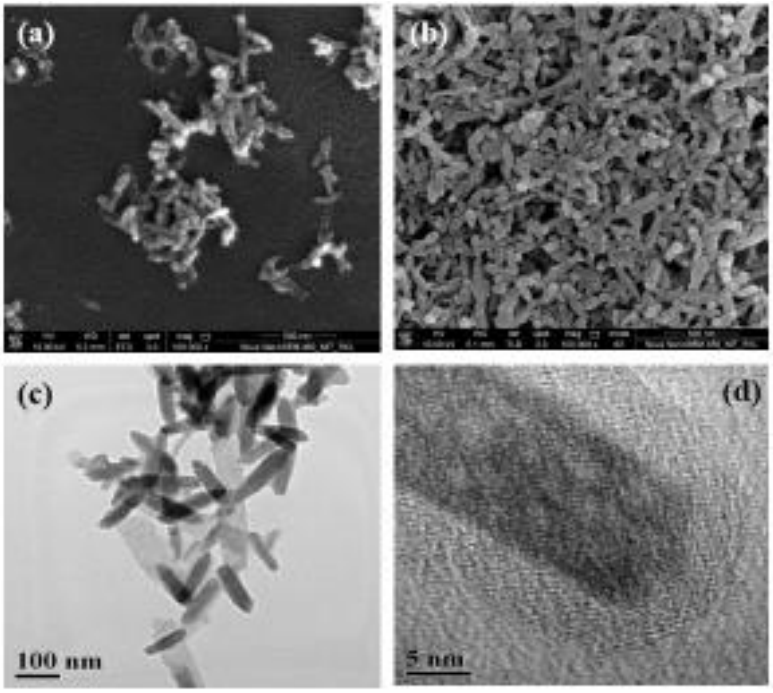

Figure 3: (a,b) FESEM, (c,d) TEM images of iron-oxide nanorods.

4.2.2 Mechanism for the formation of Iron oxide Nanorod.

The mechanism for the formation of the iron oxide nanorods may be explained as on addition of tea extract to the salt precursor, the amount of gallic acid group present in the EGCG catechins reduces the metal ions to nanoparticles thereby capping around the particle. This reaction continues till all the EGCG catechins are over. In this case, the reduced iron nanoparticles being very unstable reduces to metal oxides in a short span of time before it gets capped thereby forming iron oxides nanoparticles. The remaining excess free metal ions present in the solution may come in contact with these particles because of the difference in the surface charge. These free radicals then get reduced by the capped catechins and thereby forms a chain like structure. This mechanism

can be proved by adding more amount of tea. On addition of excess tea extract, all the metal ions get reduces by the catechins to small sized nanoparticles and are capped which prevent them from agglomeration that is understood from the morphology images taken at different concentrations.

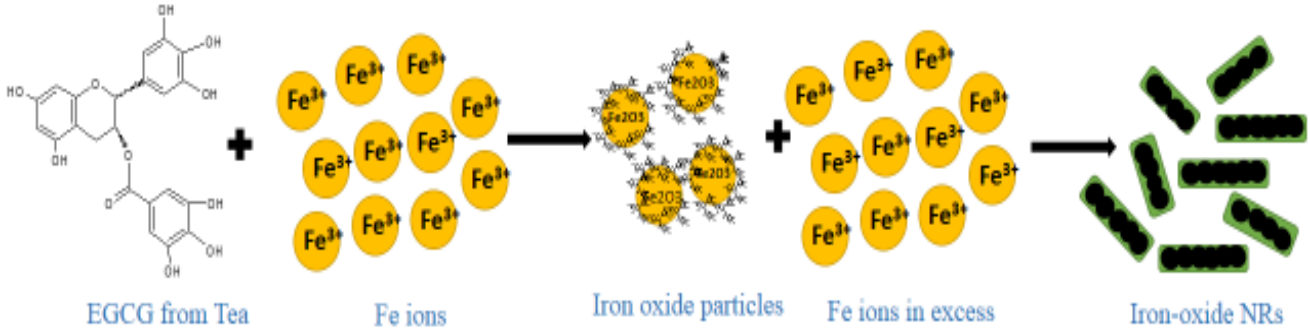

Figure 4: Mechanism of formation of Ion-oxide Nanorod

4.2.3. XRD characterization of Iron Oxide Nanorods:

The crystallinity of the sample nanorod was examined by XRD as shown in figure5. The distinct peaks were found at 26.71, 33.85, 35, 39.26, 55.85, 62.63 and 64.02° accounting for crystal planes (012), (104), (110), (113), (116), (214) and (300) respectively. The graph was compared and found to be equal to the card JCPDS no. 33-0664 of hematite. The average crystal size was found out to be 28.9nm in size by Scherrer equation.

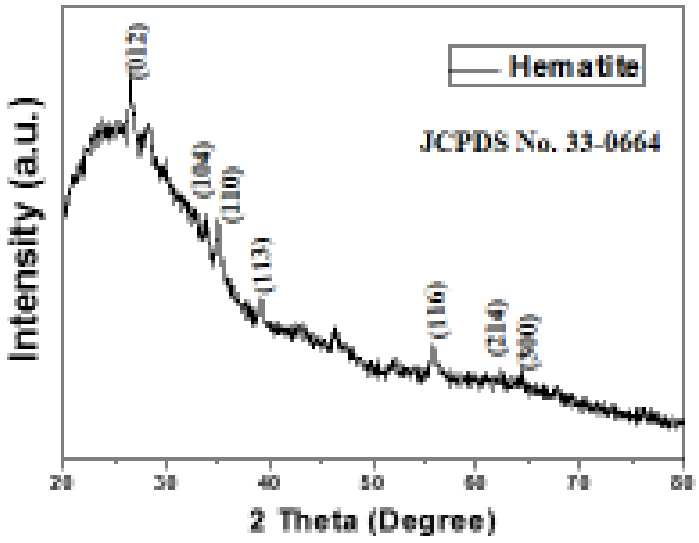

Figure 5: XRD pattern of hematite nanorod.

4.3 Au coated Iron-oxide nanorods.

Gold is used in many applications because of its surface plasmon resonance and inertness property. The properties and the performance of the nanoparticles depend upon the size of the particle. But the disadvantage of gold is the reusability of gold decreases below the size of 10nm. To overcome this problem supported catalyst method is used where the gold is coated with other metals.

4.3.1 Morphology study of Au coated iron-oxide nanorods:

The size and the morphology of the synthesized product were confirmed to be Au coated Iron Oxide Nanorods by FESEM as shown in Figue6. It is well seen that the nanorods are coated with the particles of gold have a particle size of 20nm as shown in figure6 (b). The length of the nanorod was found to be 200nm.

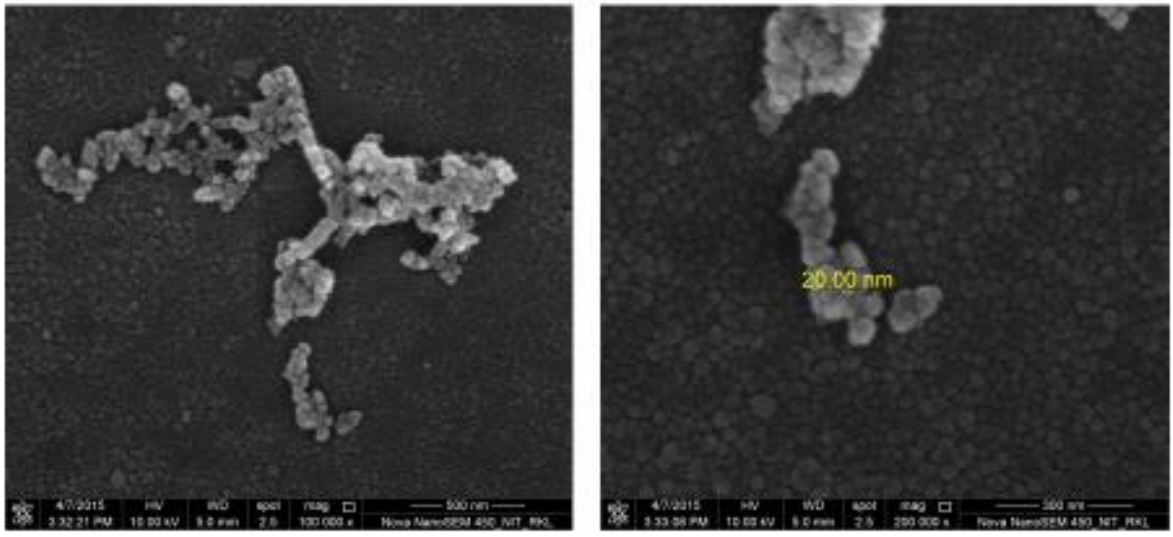

Figure 6: (a,b) FESEM image of Au coated Iron-oxide Nanorods.

4.3.2 Mechanism for the formation of Au coated Iron-oxide Nanorod.

The mechanism for the formation of the Au coated iron oxide nanorods may be explained as on addition of tea extract to the salt precursor, the amount of gallic acid group present in the EGCG catechins reduces the metal ions to nanoparticles thereby capping around the particle. The same mechanism gets carried out that of iron oxide nanorod. From the TEM image at nanorod as it was

found that there was a coating of polyphenols, on the addition of gold these polyphenols reduces the gold and thus get coated around the iron-oxide nanorod.

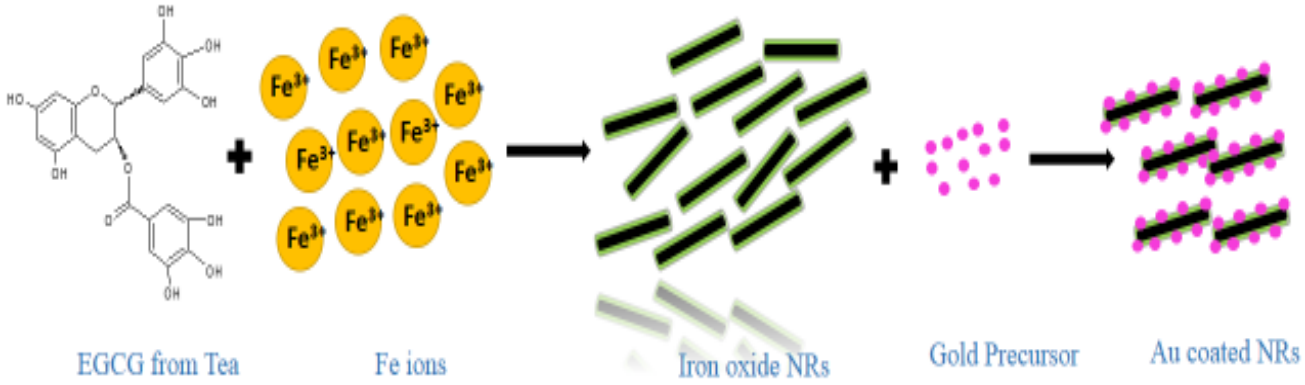

Figure 7: Mechanism of formation of Au coated Iron oxide Nanorod

4.4.3. XRD characterization of Au coated Iron-oxide Nanorods:

The crystallinity of the sample nanorod was examined by XRD as shown in figure8. The distinct peaks were found at 10.55, 17.82, 27.08 and 34.74° accounting for crystal planes (110), (200), (130), and (400) respectively for the iron-oxide which equals with the card JCPDS No. 75-1594 . The crystal planes were also found in the graph at 38.63, 44.95, 65.38 and 77.99º accounting for crystal planes (111), (200), 220) and (311) respectively. It was compared and found to be equal to the card JCPDS no. 65-2870 which represents the values for the gold. The average crystal size was found out to be 14nm for gold and 57nm in size for iron oxide by Scherrer equation.

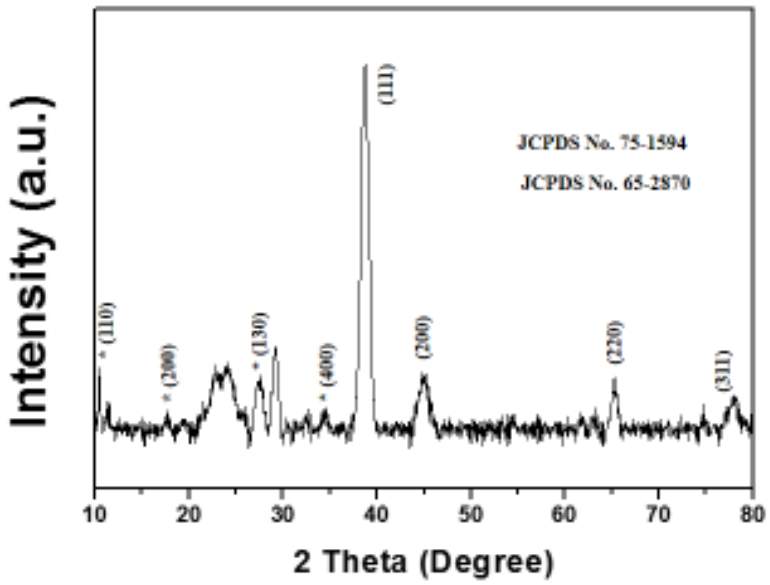

Figure 8: XRD pattern of the Au coated Iron Oxide Nanorods.

4.4 Iron-oxide tubes

Iron oxide tubes are made from different methods. Out of which the template basis is the commonly used method. There the hollow tubes are prepared by heat treatment basis having a high surface to volume ratio and magnetic in nature. Due to these properties, tubes are used in many applications such as lithium-ion batteries, Catalyst, etc. For the magnetic properties, they can be easily removed and reused. In this method, we have used the cotton as the template for the synthesis of the hollow, magnetic tubes for the application of reduction of organic compounds.

4.4.1 Morphology study of iron-oxide tubes:

The size and the morphology of the synthesized product were confirmed to be tube by FESEM shown in Figue9. The tubes are of the hollow shape of length around 100µm and width less than 1µm.The figure also revealed that the thickness of the prepared hollow tube is very thin as in figure 9(b).

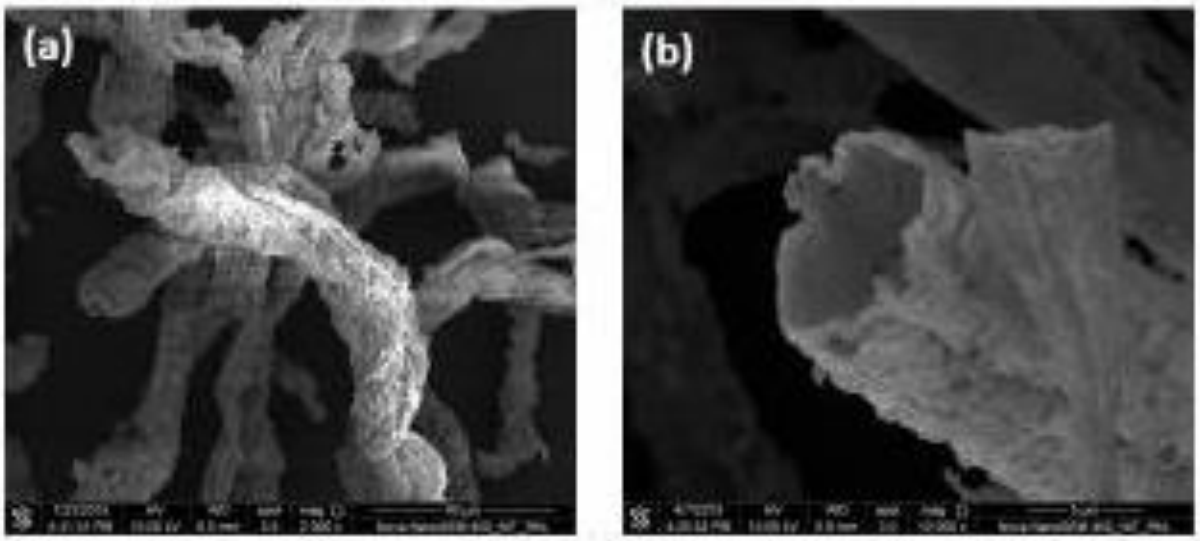

Figure 9: (a,b) FESEM image of the prepared iron-oxide tubes.

4.4.2Mechanism for Formation of Iron oxide tubes:

The formation of the tubes can be explained as when the tea is added to the cotton that have a hydrophilic surface, gets adsorbed at the surface of the cotton. In addition of the salt precursor the catechins mainly Epigallocatechin gallate (EGCG) present in the tea extract reduces the salt to metal ion on the surface of the cotton thereby forming a layer of reduced metal on the surface of the cotton. In this case, as the zero valent iron is very much unstable it gets reduces to corresponding metal oxides. On heating the sample in the furnace at 450°C, the above layer gets dried, and the cotton that is present gets burnt out giving the required hollow tube of iron oxide. The synthesized hollow iron oxide tube provided a good average surface area that was calculated by BET in the presence of Nitrogen that was having a surface area of 72 m^2/g.

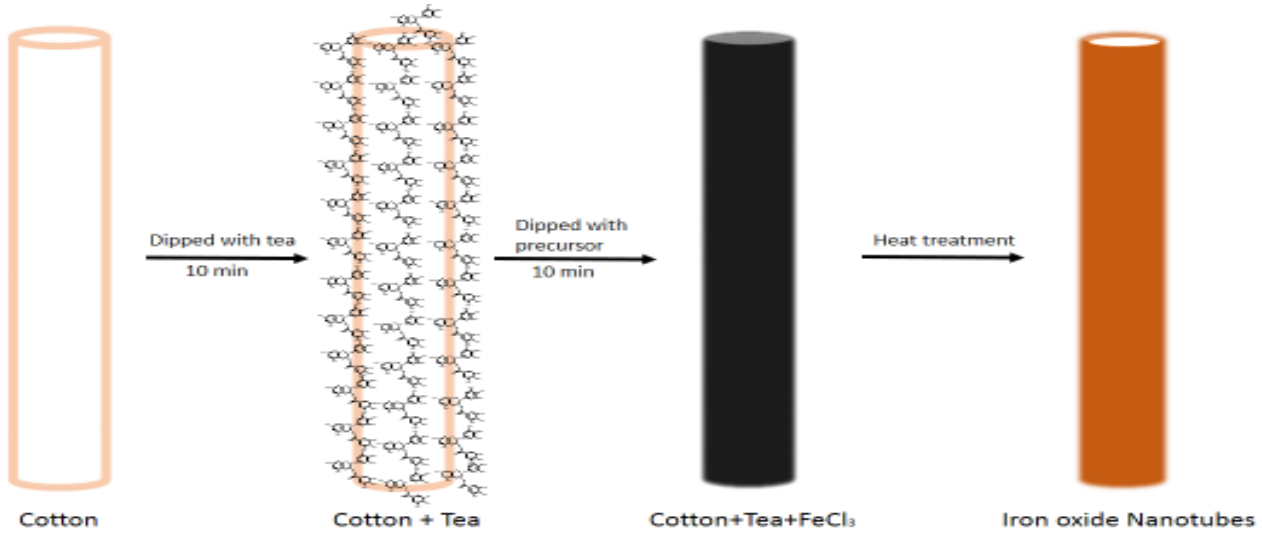

Figure 10: Mechanism for formation of Iron oxide tubes

Figure 11: Magnetic property of the iron-oxide tube.

4.4.3. XRD characterization of Iron oxide tubes:

The crystallinity of the sample nanorod was examined by XRD as shown in figure12. The distinct peaks were found at 28.98, 41.20, 50.61, 59.21 and 66.73° accounting for crystal planes (200), (400), (422), (511) and (440) respectively. The graph was compared and found to be equal to the card JCPDS no. 19-0629 which is of Fe_3O_4. The average crystal size was found out to be 23.4nm in size by Scherrer equation.

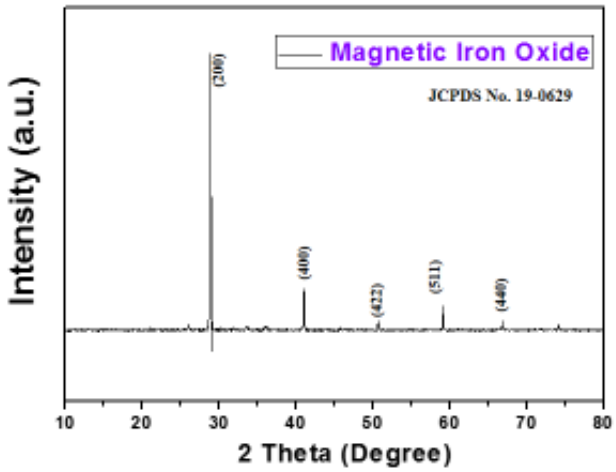

Figure 12: XRD Pattern of Iron oxide tubes.

CHAPTER-5

Applications

5.1 *Degradation of Methylene Blue by Fenton-like Catalyst:*

The need for the purification of the waste water is of great concern to today's world. The water gets polluted by various ways. Pollution by the dye is one of these factors. The water containing organic pollutants such as dyes coming out from textile industries affects the biological cycle mainly photosynthesis in aquatic plants and also makes unfit for human use and also for the marine animals. Many studies have shown that some of the dyes can also be carcinogenic and mutagenic. In this study, we have synthesized an eco-friendly method of treating these pollutants on a large scale and make then free from this pollutant free for different uses.

The sample that was collected at the regular interval was characterized by the UV-vis spectroscopy. The peak of the MB dye is found at 665nm. With the increase in the reaction time the intensity of the peak gradually decreases and at 80 min of the reaction the peak at 665nm nearly vanishes. It indicates that the total MB present in the solution has been degraded as shown in figure13.

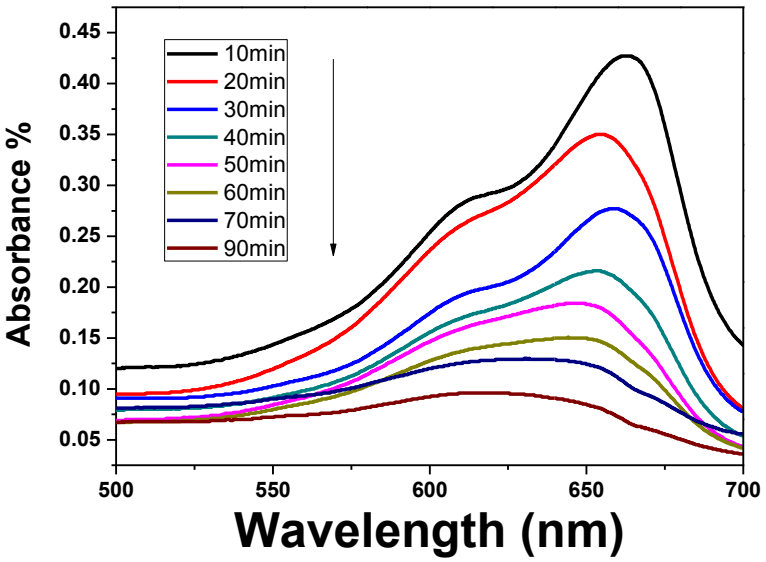

Figure 13: UV-vis spectroscopy for degradation of Methylene Blue.

The dye degradation was carried in the presence of H_2O_2. When H_2O_2 is added to the catalyst and dye solution, the Fenton-like reactions take place. The Fe^{2+} ions react with H_2O_2 to form

free radicals HO• and Fe^{3+}. This Fe^{3+} again reacts H_2O_2 to form highly oxidizing radicals HOO•. These radicals formed help in degrading the MB. The process continues till all the organic materials get degraded. The complete reaction of Fenton catalyst has been shown below.

$$\mathbf{Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO\bullet + OH^-} \cdots\cdots\cdots\cdots\cdots\cdots\cdots \mathbf{(2)}$$

$$\mathbf{Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HOO\bullet + H^+} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\mathbf{(3)}$$

The degradation process involved three steps. These are (i) Adsorption of MB on the surface of the iron-oxide tube catalyst, (ii) Reaction of the hydroxyl ions with MB and (iii) Desorption of the degraded MB from the surface to the solution. The mechanism can be given by as with increase the time of the reaction, the hydroxyl ions break the bond of MB and thus changing the whole molecular structure.

5.2 *Reduction of 4-Nitrophenol*

4-Nitrophenol is a common organic pollutant in the waste water. 4-NP have many ill effect in the body of the human body such as it reacts with blood and forms methemoglobin that is responsible for causing unconsciousness. Different methods are being carried out for the purification purposes such as adsorption, photocatalytic degradation, electrochemical process, etc. 4-NP is also a starting material for the production of the 4-AP that has many applications such as anti-corrosion lubricant, hair dyeing agent, antipyretic drugs and many more. In this study, we have synthesized catalyst and reduced 4-NP to 4-AP using Au as the primary catalyst using iron-oxide as the catalyst carrier.

The confirmation of the reduction of 4-NP was done by UV-vis spectroscopy as shown in figure 14. It has been analyzed from the graph that the peak for the reactant sample i.e. the mixture of 4-NP and $NaBH_4$ has a peak at 400nm. After the completion of the reaction, the peak gets vanished confirming the reduction of 4-NP.

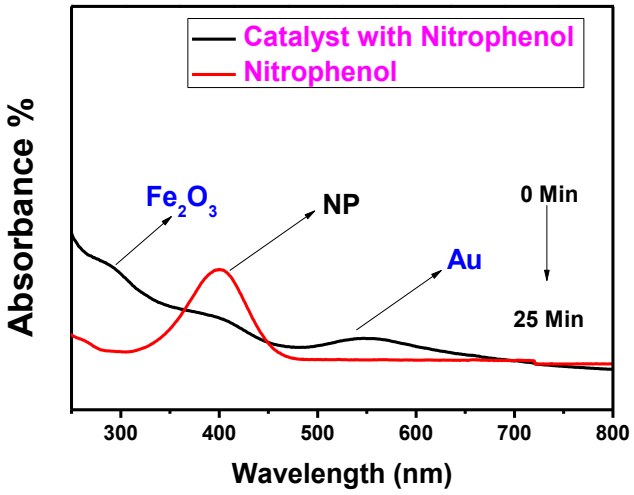

Figure 14: UV-vis spectroscopy for the reduction of 4-NP

The reduction of the 4-NP to 4-AP requires 6 electrons which are provided by $NaBH_4$ present in the sample. In water it gets dissociates to Na^+ and BH_4^-. It has been seen that even though $NaBH_4$ has higher reducing potential than that of the 4-NP still then it does not reduce the sample as shown in Figure 15. The reason behind this is of the large potential difference between the donor and the acceptor. And thus it forms a complex of 4-Nitrophenolate. So the catalyst is added to the sample to act as a bridge for the transfer of electrons from the donor to the acceptor. The reactants get adsorbed on the surface of the catalyst and thus electron transfer takes place.

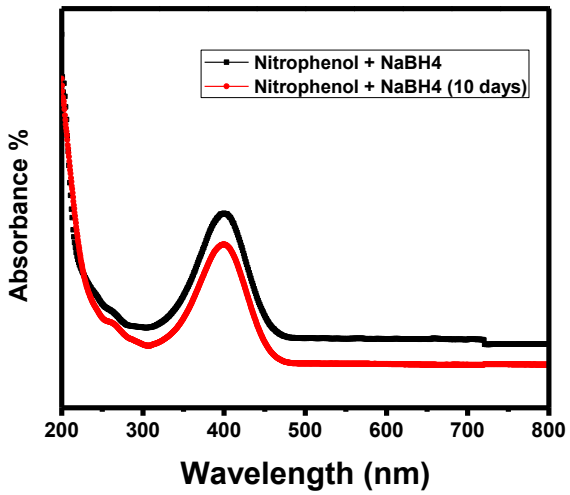

Figure 15: Rate of degredation of 4-NP without the catalyst.

Chapter 6
Conclusions

Conclusions:

In this study, we successfully synthesized nanoparticles using green tea extracts as the reducing agent. The polyphenols mainly EGCG present in the tea acts as the reducing agent as well as the capping agent. The synthesis of the nanorods were done at ambient temperature and milliseconds of time was taken for the synthesis of the Iron oxide nanorod of 20nm width with polyphenol coating around it. Iron oxide tubes were also synthesized by using cotton as the template using heat treatment method. The tubes showed a good average surface area. Tubes were used as Fenton like catalyst, where it showed a good result for the degradation of MB within 90 min which is a pollutant in the dye industry. The Au coated Fe_2O_3 nanorod were also synthesized by reducing both the metals by the help of the green tea extract. The coated Au on the iron-oxide nanorod had a size 20nm. The synthesized sample was used effectively in the reduction of 4NP to 4AP in the presence of $NaBH_4$. The time required for the reduction of the 4NP was found to be of 25min.The en result was also been found out to be 4-Aminophenol.

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